



Fabrication of hydrophobic polymer foams with double acid sites on surface of macropore for conversion of carbohydrate



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ABSTRACT

Herein we reported a simple and novel synthetic strategy for the fabrication of two kinds of hydrophobic polymer foam catalysts (i.e. Cr³⁺-HPFs-1-H⁺ and HPFs-1-H⁺) with hierarchical porous structure, inhomogeneous acidic composition and Lewis–Brønsted double acid sites distributed on the surface, which was used to one-pot conversion of carbohydrate (such as cellulose, glucose and fructose) to a key chemical platform (i.e. 5-hydroxymethylfurfural, HMF). The water-in-oil (W/O) high internal phase emulsions (HIPEs), stabilized by both Span 80 and acidic prepolymers as analogous particles offered the acidic actives, were used as the template for simultaneous polymerization of oil phase in the presence of divinylbenzene (DVB) and styrene (St). After subsequent ion-exchange process, Lewis and Brønsted acid sites derived from exchanged Cr³⁺ and H⁺ ion were both fixed on the surface of cell of the catalysts. The HPFs-1-H⁺ and Cr³⁺-HPFs-1-H⁺ had similar hierarchical porous, hydrophobic surface and acid sites (HPFs-1-H⁺ with macropores ranging from 0.1 μm to 20 μm, uniform mesopores in 14.4 nm, water contact angle of 122° and 0.614 mmol g⁻¹ of Brønsted acid sites, as well as Cr³⁺-HPFs-1-H⁺ with macropores ranging from 0.1 μm to 20 μm, uniform mesopores in 13.3 nm, water contact angle of 136° and 0.638 mmol g⁻¹ of Lewis–Brønsted acid sites). It was confirmed that Lewis acid sites of catalyst had a slight influence on the HMF yield of fructose came from the function of Brønsted acid sites, and Lewis acid sites were in favor of improving the HMF yield from cellulose and glucose. This work opens up a simple and novel route to synthesize multifunctional polymeric catalysts for efficient one-pot conversion of carbohydrate to HMF.

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1. Introduction

Increasing attention of environmental issues and environment protection urges us to accelerate the ratio of use of renewable energy and products. In nature, abundant biomass resources have the potential to occupy the main position as feedstocks, particularly as renewable carbon sources for production of fuels and chemicals (Chheda, Huber, & Dumesic, 2007). Recently, many biomass resources have been converted by effective methods into various useful products, such as 2,5-furandicarboxylic acid (FDA) (Gao, Deng, Zheng, Liu, & Zhang, 2015a), 5-hydroxy-4-keto-2-pentenoic acid (Rosatella, Simeonov, Frade, & Afonso, 2011), as well as the promising fuel 2,5-dimethylfuran (Lichtenthaler, 2002) and 5-hydroxymethylfurfural (HMF) (Wan, Lian, Wang, & Ma, 2015).

Among them, HMF, as a commonly used platform chemical, plays an important role in the bio-based energy. In terms of the production of HMF, many efforts have been focused on catalyzing carbohydrate-based biomass such as fructose and glucose due to their simple Conversion process (Li et al., 2013; Wang, Wu, Liu, Yang, & Dong, 2013; Wang, Zhang, Zhu, Meng, & Xiao, 2013). In the present available catalysts, solid acid especially porous solid acid materials (He, Bai, Jiang, & Zhou, 2013; Jiménez-Morales, Moreno-Recio, Santamaría-González, Maireles-Torres, & Jiménez-López, 2015; Lanzafame, Temi, Perathoner, Spadaro, & Centi, 2012), were widely applied in conversion of carbohydrate into HMF due to excellent thermal stability, adjustable pore sizes, high specific surface area, lower density, high catalytic activity and environmentally friendly nature.

Meanwhile, huge efforts have been focused on improving the HMF yield based on the possible mechanism of the conversion of carbohydrate-based biomass such as glucose to HMF (Atanda, Mukundan, Shrotri, Ma, & Beltramini, 2015; Xu et al., 2015; Yuan,

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Zhang, Zheng, & Lin, 2015). Recently, Scott's group synthesized the TESAS-SBA-15 catalyst by incorporating 3-((3-(trimethoxysilyl)propyl)thio) propane-1-sulfonic acid (TESAS) into SBA-15-Type Silica, meanwhile, it was found that thioether-containing TESAS-SBA-15 with more hydrophobic showed higher HMF yield (71%) than its sulfone derivative in the dehydration of aqueous fructose, and the reason may be that HMF was easy to degrade into other products in hydrophilic acid system, resulting in the low HMF yield (Crisci et al., 2011). In addition, Choudhary et al. discovered that Lewis acid (i.e. CrCl_3) catalyst was an efficient catalyst for aldoses (glucose) isomerization to ketoses (fructose) in aqueous media, and the HMF yield from aldoses (glucose) can be significantly improved by using the combined Lewis and Brønsted acid catalyst (Choudhary et al., 2013). Moreover, Auroux's group disclosed that improving ratio of catalytic active sites by using inhomogeneous acidic composition, such as Lewis–Brønsted acid sites, was a key factor for accelerating HMF yield from carbohydrate (Stosic, Bennici, Rakic, & Auroux, 2012). Therefore, the catalyst possessed hydrophobic, Lewis–Brønsted acid sites, inhomogeneous acidic composition and hierarchical porous structure may be the excellent candidate to efficiently improve HMF yield from carbohydrate. Unfortunately, it is still a serious challenge to design the multifunctional catalyst with the porous structure, binary acid sites, inhomogeneous acidic composition and hydrophobic surface. Nowadays, three main strategies are commonly used to synthesize multifunctional catalyst so as to improve the product's yield: (1) precisely control the geometry and wettability of catalyst (Zhang et al., 2013); (2) fabricate the catalyst with functional groups or active sites (Sadakiyo, Yamada, & Kitagawa, 2014); (3) change the distribution of material component to increase the utilization ratio of catalytic active sites (Rumpel & Koegel-Knabner, 2011). Although all the methods developed are attractive, creating one technique embodying all three strategies mentioned above, would be a great significant approach for meeting requirements of the real-world application, and also be a breakthrough in synthetic ways of material science.

In our recent work (Gao et al., 2015b), the acid-base polymeric catalysts with hydrophobic, hierarchical porous structure were synthesized. But there were two problems still posed a serious challenge in this field. Firstly, the use of 98 wt% H_2SO_4 in sulfonating process to gain acidic sites was a disadvantage factor to environment and instrument, and it was also difficult to control the amount of acidic sites via this method. Secondly, the utilization ratio of catalytic acidic active sites was low. However, only the acidic active sites on the catalysts surface were able to catalyze the reaction. The uniform distribution of acidic active sites in catalyst were commonly produced by sulfonation process, and the acidic active sites in the inter layer of catalyst were unavailable. Recently, many studies about novel Pickering HIPes, adopting both particles and few polymeric surfactants as emulsifier, created various functional materials with open porous structure and greatly enhanced permeability (Ikem, Menner, Horozov, & Bismarck, 2010). In these works, particles distributed at the interface of oil and water were used to be main emulsifier to form HIPes. After the polymerization process of external phase, particles were embedded at the surface of macroporous polymers. Meanwhile, acidic polymer synthesized by copolymerizing the oil-solubility and acidic water-solubility monomer will avoid the sulfonating process to obtain acidic sites, and the acid content can be effectively control via changing acidic water-solubility monomer (Wang et al., 2014). Based on above analysis, the acidic crosslinked prepolymer ingredients, as analogous particles prepared by copolymerizing the oil-solubility and acidic water-solubility monomer in advance, may be mixed with the monomer of oil phase to form stable Pickering W/O HIPes. Thus, acidic crosslinked prepolymer may be endowed another new role exception to the emulsifier, such as acidic actives on the external surface,

which would improve the utilization ratio of catalytic acidic active sites and accord with the requirement of green chemistry.

Additionally, our group fabricated the Lewis–Brønsted acid sites via two steps; firstly, $-\text{SO}_3\text{H}$ were grafted on surface of Halloysite via silane-coupling reaction with 3-(mercaptopropyl)trimethoxysilane and oxidization of H_2O_2 , then ion exchange with Cr^{3+} , offering a way to how build the Lewis–Brønsted acid sites and verifying the efficient catalytic active of Lewis–Brønsted acid sites (Zhang, Pan, Gan, et al., 2014b). Inspired by the information mentioned above, two kinds of hydrophobic polymer foams (i.e. Cr^{3+} -HPFs- H^+ and HPFs- H^+) with hierarchical porous structure, inhomogeneous acidic composition and Lewis–Brønsted acid sites were successfully designed and synthesized by W/O HIPes template method and subsequent ion-exchange process with H^+ and Cr^{3+} (Scheme 1). Firstly, as-prepared acidic crosslinked prepolymer ingredients as analogous particles and few span 80 were used to stabilize W/O Pickering HIPes with an internal phase volume ratio of 84.8%. Then, HIPes, possessed the continuous oil phase containing St and DVB monomer and internal phase comprising of K_2SO_4 aqueous solution, were applied to fabricate hydrophobic porous foams (HPFs). After ion-exchange in H^+ and Cr^{3+} , Cr^{3+} -HPFs- H^+ and HPFs- H^+ were obtained, respectively. Moreover, the amount of acid and the amount of acidic type with Lewis–Brønsted were controlled by adjusting the content of acidic crosslinked prepolymer ingredients and the concentration of Cr^{3+} and H^+ , respectively. Finally, obtained Cr^{3+} -HPFs- H^+ and HPFs- H^+ were both characterized, and their catalytic activities were explored in detail under optimizing the reaction time, temperature and loading amounts in catalyzing carbohydrate (fructose, glucose, and cellulose) to HMF.

2. Material and methods

2.1. Materials

All of the chemicals, 1-ethyl-3-methyl-imidazolium chloride ([EMIM]-Cl), $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, HCl, sodium p-styrene sulfonate (SS, 99%), cellulose (powder, ca. 50 μm), glucose, fructose, 5-hydroxymethylfurfural (HMF, >99%), styrene (St, 99.9%), divinylbenzene (DVB, 80%), tetrahydrofuran (THF, 99.9%) were supplied from Aladdin reagent CO., LTD (Shanghai, China). 2,2'-azobis (2-methyl-propionitrile) (AIBN, 99%), Span 80, K_2SO_4 , and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals were purchased by local suppliers and used without further purification.

2.2. Fabrication of Cr^{3+} -HPFs- H^+ and HPFs- H^+

Cr^{3+} -HPFs- H^+ and HPFs- H^+ were synthesized by polymerization reaction and subsequent ion-exchange process. The first step was the fabrication and polymerization of a stable W/O Pickering HIPes. Firstly, the mixtures including DVB (2.0 mL), AIBN (50 mg), SS (1.0 g), H_2O (8.0 mL), and THF (20 mL) were polymerized at 60 °C for 3.0 h under stirring. After evaporation of THF at room temperature, the prepolymer mixtures were obtained. Secondly, a mixed phase, containing the organic phase and aqueous phase, was formed by adding the aqueous phase and oil phase under a fast and continuous mechanical stirring at 400 rpm for over 10 min. The oil phase was consisted of DVB (1.0 mL), St (1.0 mL), Span 80 (0.6 mL) and as-prepared prepolymer, while the aqueous phase included 12 mL of double distilled water and 80 mg of K_2SO_4 . After the emulsification, a stable W/O Pickering HIPes was formed. Then the obtained HIPes were transferred into a plastic centrifuge tube, and they were polymerized in a circulating air oven at 60 °C for 12 h. Finally, polymerized HIPes monoliths (i.e. HPFs) were washed

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